η-CYCLOHEPTATRIENYL-MOLYBDENUM CHEMISTRY: TERTIARY PHOSPHINE, ALKYL, HYDRIDO, HALOGENO AND RELATED DERIVATIVES

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Abstract—The preparation and properties of the compounds $[Mo(\eta-C_7H_7)(dppe)Y]$ (Y = Cl, I, Me, H), $[Mo(\eta-C_7H_7)(dppe)Cl]^+A^-$ (A = PF₆, Br or I), { $[Mo(\eta-C_7H_7)(dppe)Br]PF_6$ }, { $[Mo(\eta-C_7H_7)(dppe)I]PF_6$ } and { $[Mo(\eta-C_7H_7)(dppe)L]PF_6$ } (L = CO, MeCN, or dppe) are described.

The functional group properties of the η -bonded η -C_nH_n ligands, where n = 4-8, in their transition metal complexes are best determined by an exploratory synthetic approach followed by a more quantitative study. As part of a development of the chemistry of the η -C₇H₇ ligand we have set out to study derivatives of the system [Mo(η -C₇H₇)(dppe)].

Prior to this work and during the course of these studies there have been reports of other η -C₇H₇molybdenum compounds.¹ In particular, the reactions of $[Mo(\eta-C_7H_7)(CO)_3]BF_4$ have been studied in considerable detail.^{2,3} The η -C₇H₇ ring of this cation undergoes nucleophilic addition, e.g. of P(Prⁱ)₃,⁴ CN⁻, OMe⁻ and Ph⁻,⁵ whilst displacement of carbon monoxide with dppe gives [Mo(η - C_7H_7)(dppe)CO]BF₄.⁶ Substitution of one CO group by halides ions, X = Cl, Br or I, forms the neutral $Mo(\eta-C_7H_7)(CO)_2X^7$ Treatment of the latter with tertiary phosphines causes successive replacement of the two CO groups⁸ whilst with cyclopentadienide salts the compound $Mo(\eta^3 C_7H_7$)(CO)₂(η -C₅H₅) is isolated.⁹ The compound $[Mo(\eta-C_7H_7)(CO)_3]BF_4$ reacts under photolysis with arenes giving the mixed sandwich compounds $[Mo(\eta-C_7H_7)(\eta-arene)]BF_4$.¹⁰ However, with acetonitrile the η -C₇H₇ ring is displaced, forming Mo(MeCN)₃(CO)₃.⁵

The compounds $[Mo(\eta - C_7H_7)(\eta - arene)]A^$ readily undergo displacement of the η -arene ring leading to many derivatives and, in particular, the compounds $[Mo(\eta-C_7H_7)L_3]A$, where L = MeCN or Me₂CO.^{10,11} These solvate molecules are highly reactive towards substitution of the solvent ligands. Treatment of $[Mo(\eta-C_7H_7)(\eta-arene)]A$ with methoxide or halides forms the dimers $[(\eta-C_7H_7)Mo(\mu-X)_3Mo(\eta-C_7H_7)]$, X = OR, Cl, Br or I.^{12,13} An unusual tetrameric compound $[Mo(\eta-C_7H_7)(\mu^3-OH)]_4$ has been described.¹⁴

It appears that the $Mo(\eta-C_7H_7)$ moiety is more resistant to ring displacement and to nucleophilic addition reactions in those derivatives where CO ligands are absent.¹⁵

A preliminary communication of part of this study on the $Mo(\eta$ - $C_7H_7)$ dppe moiety has been published.¹⁶

RESULTS

Treatment of the compound

$$\{[Mo(\eta-C_7H_7)(\eta-C_6H_5Me)]PF_6\},\$$

1, in acetone or acetonitrile with one equivalent of bis-1,2-(diphenylphosphino)ethane (dppe) causes displacement of the $(\eta$ -C₆H₅Me) ligand. The acetonitrile solutions give the red crystalline compound {[Mo(η -C₇H₇)(dppe)MeCN]PF₆}, 2. The compound isolated from the acetone solution was a brown oily material. It was not found possible to either obtain consistent analyses or to isolate a crystalline sample. However, the material behaves as though it were the compound {[Mo(η -C₇H₇)(dppe)(Me₂CO)]PF₆}, 3. For example, treatment of 3 with carbon monoxide gives {[Mo(η -C₇H₇)(dppe)CO]PF₆}, 4. The compound 4 has been described previously and was prepared from [Mo(η -

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 C_7H_7)(CO)₂I], dppe and NH₄PF₆.⁸ Addition of a chloride ion to solution of 3 forms [Mo(η -C₇H₇)(dppe)Cl], 5, which crystallises from dichloromethane or toluene as green crystals which contain solvent molecules of crystallisation. The crystal structure of the compound [Mo(η -C₇H₇)(dppe)Cl] toluene has been determined and is presented in Scheme 1 (Mo-Cl, 2.52; Mo-P, 2.50, 2.49 Å).¹⁷ The ¹H NMR spectrum of both the dichloromethane and toluene solvate derivatives of 5 in C₆D₆ are anomalous since neither show bands assignable to a η -cycloheptatrienyl ligand although bands due to the dppe ligand are present.

Reduction of the hexafluorophosphate salt of the 17 electron cation $[Mo(\eta-C_7H_7)(dppe)Cl]^+$ (vide infra) with sodium amalgam in dichloromethane gave 5 in high yield. When the reduction was carried out in tetrahydrofuran solution then brown crystals were obtained whose stoichiometry also corresponded to 5 but whose ¹H NMR showed all the bands to be expected, including a triplet at δ 4.9 assignable to a η -cycloheptatrienyl group coupled to two equivalent ³¹P nuclei. The brown isomer may be a polymorph of 5.

Houk and Beall have described a compound $[Mo(\eta-C_{7}H_{7})(dppe)I]$.⁸ We have prepared a compound 6 of the same stoichiometry from the reaction between 3 and lithium iodide. Initially a light green precipitate forms which redissolves and then brown crystals of 6 separate. Also, treatment of the acetonitrile derivative 2 with lithium iodide in acetonitrile followed by recrystallisation of the involatile products from acetone gives the compound 6. The IR and NMR spectra of 6 do not correspond to that reported and, as found for the green isomer of 5, the compound 6 did not show a band in the ¹H NMR spectrum assignable to the η cycloheptatrienyl hydrogens. These anomalous absences of η -C₇H₇ resonances may be due to traces of paramagnetic impurities.

The compounds 5 and 6 are readily oxidised by iodine and, after addition of ammonium hexafluorophosphate, the paramagnetic compounds $\{[Mo(\eta-C_7H_7)(dppe)Cl]PF_6\}$, 7, and $\{[Mo(\eta-C_7H_7)(dppe)I]PF_6\}$, 8, are formed.

Addition of lithium iodide to the yellow compound 7 at room temperature resulted in an immediate reaction giving metathesis of the hexafluorophosphate anion and the blue iodide salt $\{[Mo(\eta-C_7H_7)(dppe)Cl]I, 9, was isolated. Similarly,$ treatment of 7 with lithium bromide forms the $compound <math>\{[Mo(\eta-C_7H_7)(dppe)Cl]Br\}$, 10. Prolonged reaction between 7 and lithium iodide gave 8, after addition of ammonium hexafluorophosphate.

In an unexpected reaction, it was found that

treatment of 3 with dichloromethane or allyl chloride causes oxidation forming 7. Similarly 3 undergoes oxidation in the presence of 1,2dibromoethane giving { $[Mo(\eta-C_7H_7)(dppe)Br]PF_6$ }, 11.

The ESR data for the compounds 7, 11 and 8 are given in Table 1. The spectra of the compound 7 and 11 both show hyperfine structure assignable to coupling of the unpaired electron with two equivalent ³¹P nuclei, with the ⁹⁵Mo and ⁹⁷Mo nuclei and, possibly, also with the hydrogens of the η cycloheptatrienyl ring and with either the Cl or Br nuclei. The spectra have not been fully assigned due to their complexity. The magnetic susceptibility data for the compounds 7, 9, 10 is consistent with the presence of one unpaired electron in the cations.

When 1 was treated with an excess of dppe salmonpink crystals were obtained which had a stoichiometry corresponding to $\{[Mo(\eta-C_7H_7)(dppe)_2]\}$ PF_6 , 12. The ¹H NMR of 12 in deuterioacetone or CD₃CN showed a triplet centered at δ 4.9 (J(P-H) 2.1 Hz) assignable to the η -cycloheptatrienyl hydrogens coupled to only two ³¹P nuclei. The ³¹P NMR in (CD₃)₂CO showed two bands assignable to phosphorus in dppe systems. The band at -61.4 ppm has a chemical shift value close to that of the coordinated phosphorus in 2 whilst the second band had a chemical shift value at 13.5 ppm which is close to that of uncoordinated dppe. Thus it seems that the compound 12 dissociates a dppe ligand in acetonitrile or acetone solutions. In support of this observation it was found that treatment of 12 in acetone with carbon monoxide gives the compound 4.

Reduction of 6 with sodium borohydride in tetrahydrofuran gives highly air sensitive red crystals of the hydrido compound $[Mo(\eta-C_7H_7)(dppe)H]$, 13. The compound reacts rapidly with CDCl₃ giving 5. Treatment of 6 with methyllithium in warm tetrahydrofuran gives the expected methyl compound $[Mo(\eta-C_7H_7)(dppe)Me]$, 14.

DISCUSSION

The reactions and proposed structures for the new compounds are shown in Scheme 1. The characterising data are given in Table 1.

The question of the formal oxidation state of of the molybdenum centre in these compounds arises. Recently we have reported an extensive chemistry of the η -C₇H₇Ti system^{18,19} in which we conclude that the η -C₇H₇ ligand is best described as having a formal trinegative charge so that, for example, the titanium centre in the compound Ti(η -C₇H₇)(dmpe)Cl classifies as d^0 (i.e. Ti(IV)).

By analogy, the molybdenum centre in the com-

Table 1. Analytical and spectroscopic data

Compound and colour	Analytical data (%) ^a C, H, N or Hal ^e	ESR, ¹ H NMR ^b , magnetic susceptibility data
$\frac{1}{2 \left\{ \left[Mo(\eta - C_7 H_7)(dppe)(MeCN) \right] PF_6 \right\}}$	54.4 4.3 1.7	2.5, 20 , c, 4 Ph; 4.95, 7, t(J(P-H) 2),
Red	(54.5) (4.4) (1.8)	C_7H_7 ; 7.4 and 7.55, 4, c, 2CH ₂ ; 8.5, 3, $t(J(P-H = 1), Me^{d,e})$
$5 [Mo(\eta - C_7H_7)(dppe)Cl] \cdot C_6H_5Me$	67.8 5.3 5.2	2.9, 25, c, 5 Ph; 7.9, 3, o, Me;
Green	(67.5) (5.5) (5.0)	8.0, 4, m, br, 2 $CH_2^{f,g}$
6 $[Mo(\eta-C_7H_7)(dppe)I]$	55.9 4.6 18.4	2.9, 20 , c, 4 Ph, 8.0, 4 , c, 2CH ₂ ^f
Green-brown	(55.6) (4.4) (18.0)	· · · · · · · · ·
7 {[Mo(η -C ₇ H ₇)(dppe)Cl]PF ₆ }	52.4 4.3 4.7	$\mu_{\text{eff}} = 1.26 \text{ B.M.}; \langle g \rangle = 1.992(6);$
Yellow	(5.18) (4.0) (4.6)	$a_{ino} = 23$; $a_{ino} = 5.5$; $1w.4^{j}$
8 { $Mo(\eta-C_7H_7)(dppe)I$]PF ₆ }	45.9 4.1	$\langle g \rangle = 2.056(8); 1w = 64^{k}$
Scarlet red	(46.2) (3.6)	
9 { $[Mo(\eta-C_7H_7)(dppe)Cl]I$ }	53.1 4.1 17.2	$\mu_{eff} = 0.450 \text{ B.M.}$
Blue	(53.0) (4.1) (17.0)	
10 { $[Mo(\eta-C_{7}H_{7})(dppe)Cl]Br$ }	55.7 4.6 12.0	$\mu_{\text{ref}} = 0.626 \text{ B.M.}$
Orange-yellow	(56.6) (4.1) (11.4)	
11 { $[Mo(\eta-C_7H_7)(dppe)Br]PF_6$ }	49.0 4.1 10.4	$\langle g \rangle = 2.015(8); a_{iso}(P) = 45,^{h}$
Orange-yellow	(48.9) (3.8) (9.9)	$a_{inc} = 6.3$ ⁱ 1w.7 ¹
12 { $[Mo(\eta-C_7H_7)(dppe)_7]PF_6$ }	62.3 4.9 ^m	2.45, 2.7, <i>c</i> , <i>br</i> , 8 Ph : 4.95,
Red	(62.8) (4.9)	7 . $?(J(P-H)2.1)C_7H_7$: 7.5, 8 .
		c, br, $2CH_2^{d,n}$
13 $[Mo(\eta-C_7H_7)(dppe)H]$	o	2.6, 20, c, 4 Ph; 4.9, 7, d of t
Red		$(J(P-H) 2.1, J(H-H) 1.2), C_{-}H_{-}; 7.8,$
		4. m. br. 2CH ₂ : 13.9. 1.
		$t(J(P-H) 51), Mo-H^{f}$
14 $[Mo(\eta - C_2H_2)(dppe)Me]$	68.0 5.9	3.1. 20 , c. 4 Ph. 5.5. 7 .
Red	(68.0) (5.7)	$t(J(P-H = 1.8), C_{\pi}H_{\pi}; 8.7, 4)$
	() ()	c. br. 2CH ₂ : 10.8. 3.
		$t(J(P-H) 10.5), Me^{f}$

^a Calculated values given in parentheses.

^b¹H NMR data given as : chemical shift (τ), relative intensity, *multiplicity* (J in Hz), assignment. ESR data; $\langle g \rangle$; a_{iso} in gauss, assignment; 1w. = average width of main lined (gauss).

° Not fluorine.

^d In $(CD_3)_2CO$.

 $^{\circ 31}$ P NMR in CD₃CN: 65.5 (dppe); 144.5, 7 lines (J(P-F) 705.6), PF₆. Specific conductance in CH₂Cl₂ = 0.395 mho cm⁻². The CN stretch was at 2275w.

 f In C₆D₆.

⁸ The mass spectrum shows a parent ion peak at m/e = 622 (⁹⁶ Mo).

^h Coupling to two equivalent ³¹I nuclei (gauss).

³Coupling to ³⁵Cl and ³⁷Cl and possibly to the hydrogens of the C₇H₇ ring (gauss).

^j In acetone : methanol (1 : 1).

¹In acetone.

^m Mo, 8.5 (8.1); P, 13.7 (13.1)%.

^{n 31}P NMR in (CD₃)₂CO: -61.4, 13.5, dppe; 144, 5₄ septet (J(P-F) 705.6), PF₆.

^o The stoichiometry was determined by the mass spectrum, m/e = 588 (⁹⁶Mo), corresponding to the parent ion.

pounds of the type $Mo(\eta-C_7H_7)L_2X$, and $[Mo(\eta-C_7H_7)L_3]^+$, where L = a two electron donor, and X = a one electron donor (e.g. Cl, Me), are described as d^2 , i.e. Mo(IV). Correspondingly, the paramagnetic compounds $[Mo(\eta-C_7H_7)L_2Cl]^+$ are d^1 with Mo(V). This accounts for the observation of ESR

spectra which are most characteristic of the presence of only one unpaired electron.

The observed reactivity of the $Mo(\eta-C_7H_7)$ moiety is consistent with this description. For example, the extreme lability of the η -arene ring in $[Mo(\eta-C_7H_7)(\eta$ arene)]⁺ and its facile displacement by relatively



Scheme 1.

- (i) Dppe (1 equiv.) in acetonitrile at 65°C for 12 h, 74%.
- (ii) Dppe (1 equiv.) in acetone at 65°C for 11 h, ca 50%.
- (iii) Dissolve in acetonitrile at 20°C, 10 min, > 90%.
- (iv) Excess of lithium iodide in acetonitrile at 20°C, 10 min, > 90%.
- (v) Dppe (2 equivalent) in ethanol at 60°C for 24 h, > 90%.
- (vi) Carbon monoxide at 1 atm in acetone at 20°C for 3 h, 42%.
- (vii) Halides = Cl, Br or I. Lithium halides in acetone at 20°C for 30 min, > 70%.
- (viii) X = Cl, dissolve in CH_2Cl_2 or allylchloride at room temperature for 10 min, > 90%.
- X = Br, dissolve in 1,2-dibromoethane at room temperature for 15 min, > 90%.
- (ix) X = Cl or I, add iodine at room temperature for 10 min, > 90%.
- (x) X = Cl, stir with Na/Hg in CH_2Cl_2 at room temperature for 1 h, > 90%.
- (xi) X = I, Na[AlH₂(OCH₂CH₂OMe)₂] in toluene at 80°C for 1 h, 72%.
- (xii) Methyllithium in toluene at 80°C for 1 h, 42%.

"hard" ligands such as halide, methoxide, acetone and MeCN is more consistent with a d^2 than a d^4 , or, if the η -C₇H₇ ligands was thought to classify as C₇H₇⁺, as a d^6 centre. The compound [Mo(η -C₇H₇(CO)₂I] undergoes displacement of both CO ligands by the more strongly donor tertiary phosphine ligands.⁸ In contrast, the CO ligands in the d^4 compounds [Mo(η -C₅H₅)(CO)₃X] are much less labile. = OMe, Cl, Br, I, may be regarded as having formal d^0 centres, if a Mo-Mo bond is assumed, and reduction to the neutral paramagnetic compounds $[(\eta-C_7H_7)Mo(\mu-X)_3Mo(\eta-C_7H_7)]$ would provide a formal d^1 molybdenum centre, which is consistent with the observed ESR data.^{12,13}

The chemistry of the system $[Mo(\eta-C_7H_7)(dppe)]$ compares generally with that of the well-known $Fe(\eta-C_5H_5)L_2$ -moiety, for example, in the formation of the hydrido and alkyl derivatives.

The dimers $[(\eta - C_7 H_7)Mo(\mu - X)_3Mo(\eta - C_7 H_7)]$, X

EXPERIMENTAL

All preparations and reactions were carried out under an atmosphere of purified dinitrogen. Solvents were dried and purified by reflux over a suitable drying agent under dinitrogen, followed by distillation under dinitrogen. Microanalyses were performed by the analytical department of this laboratory or by Alfred Bernhardt Ltd.

IR spectra were recorded on a Pye–Unicam SP2000 double beam, grating spectrophotometer or a Perkin–Elmer 457 double beam, grating spectrophotometer.

NMR spectra were recorded on a JEOL PMX60 (¹H, 60 MHz), a Bruker WH90 (¹H, 90 MHz; ³¹P, 36.43 MHz). Solvent bands were used as internal standards. Mass spectra were recorded on an A.E.I. MS 902 spectrometer. ESR spectra were determined on a JEOL JES-PE instrument at 9.5 GHz and calibrated against MnO as external standard.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)acetonitrilemolybdenum hexafluoro - phosphate, **2**

The compound { $[Mo(\eta-C_7H_7)(\eta-C_6H_5Me)]PF_6$ } (1.0 g, 2.36 mmol), prepared as described, ¹² and dppe (0.91 g, 2.34 mmol) in acetonitrile (40 cm³) were heated at 65°C for 12 h. The solution was concentrated under reduced pressure at 70°C and allowed to cool. Red crystals separated and were collected washed with tolucne and dried under reduced pressure. Yield 74%.

Synthesis of 3 from $\{[Mo(\eta-C_7H_7)(\eta-C_6H_5Me)] PF_6\}$

The compound

$\{[Mo(\eta-C_7H_7)(\eta-C_6H_5Me)]PF_6\}$

(0.76 g, 1.8 mmol) in acetone (20 cm³) was treated with 1,2-bis(diphenylphosphino)ethane (0.71 g, 1.8 mmol) at 65°C for 11 h. The solvent was removed under reduced pressure and the brown frothy residue of the material 3 was used without further purification in the reactions described below, yield 1.55 g. [Found : C, 54.6 (54.9); H, 6.0 (4.7)%.] Crystals obtained from concentrated acetone solutions analysed as C, 52.6 (54.9); H, 5.1 (4.7)%.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)carbonylmolybdenum hexafluorophosphate, **4**

Method A. The compound 3 (0.3 g, 0.38 mmol) in acetone (5 cm^3) was treated with carbon monoxide at

1 atm for 3 h. The initially brown solution became red. Ethanol (20 cm^3) was added and the solution was concentrated under reduced pressure giving red crystals. These were recrystallised twice from dichloromethane: petroleum ether (40–60°C) mixture. The resulting red crystals were washed with petroleum ether (40–60°C) (2 × 10 cm³) and dried *in* vacuo, 0.12 g, 42%. The compound was identified by analysis. [Found (calc.): C, 53.6(53.9); H, 3.9(4.1)%.] Specific conductance in CH₂Cl₂ was 0.435 mho cm⁻². The IR spectrum was identical to that described (the CO stretch was at 1952vs cm⁻¹).

Method B. The compound

 ${[Mo(\eta-C_7H_7)(dppe)_2]PF_6}$

(0.07 g, 0.06 mmol) in dicholoromethane (5 cm⁻³) was treated with carbon monoxide at 1 atm and at room temperature for 5 h. The solvent was removed under reduced pressure and the residue was recrystallised from acetone: ethanol mixture. The resulting crystals were washed with petroleum ether $(40-60^{\circ}C)(2 \times 10 \text{ cm}^3)$ and dried *in vacuo*, 0.023 g, *ca* 50%.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)chloromolybdenum, 5

Method A. The compound 3 (0.2 g, 0.25 mmol) in acetone (10 cm³) was treated with lithium chloride (0.2 g, 4.8 mmol) in acetone (20 cm³). The initially brown solution turned green. After 2 h the solvent was removed under reduced pressure and the residue was extracted with toluene (10 cm³). The extract was filtered and petroleum ether (100–120°C) was added to the filtrate. Concentration of the mixture under reduced pressure gave green needle crystals which were collected and dried *in vacuo* 0.13 g, 72%.

Method B. The compound {[$Mo(\eta-C_7H_7)$ (dppe)Cl]PF₆} (0.5 g, 0.65 mmol) in dichloromethane (40 cm³) was treated with sodium amalgam (10 g of 2% sodium in mercury) and stirred for 1.5 h. The mixture was allowed to stand for 2 h and the green supernatant solution was separated by filtration and the filtrate was treated with petroleum ether (60-80°C: 60 cm³). After concentration under reduced pressure green crystals separated over a period of several days, 0.2 g, 44%. [Analytical data for [$Mo(\eta-C_7H_7)$ (dppe)Cl] $\cdot \frac{1}{2}CH_2Cl_2$: Found (calc.): C, 57.9(57.9); H, 4.6(4.6); Cl, 14.9(15.1)%.]

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)iodomolybdenum, **6**

A solution of the compound 3, prepared from 1 (0.50 g, 1.18 mmol) in acetone (5 cm³) and dppe (1 equivalent) in acetone (5 cm³) was treated with

anhydrous lithium iodide (0.5 g, 3.75 mmol) in acetone (10 cm³). Fibrous green crystals separated immediately but after 15 min these redissolved and a new precipitate of brown lustrous cubic crystals separated. These were collected, washed with acetone ($2 \times 5 \text{ cm}^3$) and dried *in vacuo*, 0.73 g, *ca* 87%. The specific conductance in CH₂Cl₂ was 0.0094 mho cm⁻². The mass spectrum showed a parent ion peak at *m/e* = 714.

The compound could be recrystallised from toluene: petroleum ether $(100-120^{\circ}C)$ mixture as yellow-green fibrous crystals whose IR spectrum differed slightly from that of the brown-green cubic crystals.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclohepta - trienyl)chloromolybdenum hexafluorophosphate, 7

Method A. The compound 3 (0.5 g) was dissolved in dichloromethane (20 cm³). After 15 min at room temperature the solution was yellow-orange. The solvent was removed under reduced pressure and the residue was recrystallised from acetone: ethanol mixture, ca 90%.

Method B. The compound

$[Mo(\eta-C_7H_7)(dppe)Cl]$

(0.1 g, 0.16 mmol) in dichloromethane was treated with iodine (0.2 g, 0.7 mmol). Addition of petroleum ether (60–80°C) followed by concentration under reduced pressure precipitated black crystals. These were separated and dissolved in aqueous acetone. Aqueous ammonium hexafluorophosphate was added and the mixture was concentrated giving yellow crystals which were collected and dried *in* vacuo, ca 90%.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)iodomolybdenum hexafluorophos - phate, **8**

The compound $[Mo(\eta-C_7H_7)(dppe)I]$ (0.18 g, 0.25 mmol) in toluene (80 cm³) was treated with one equivalent of iodine in toluene (10 cm³) giving a black precipitate. This was collected and extracted with aqueous acetone. The extract was filtered and aqueous ammonium hexafluorophosphate was added. The filtrate was concentrated under reduced pressure giving scarlet red crystals. These were recrystallised from dichloromethane : petroleum ether (40–60°C), yield 90%.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)chloromolybdenum iodide, 9

The compound { $[Mo(\eta-C_7H_7)(dppe)Cl]PF_6$ }, 7 (0.2 g, 0.26 mmol), was treated with anhydrous

lithium iodide (0.5 g, 3.7 mmol) in acetone (10 cm³). Blue crystals separated and after 4 h these were collected, washed with ethanol and dried *in vacuo*, *ca* 72%.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)chloromolybdenum bromide, 10

The compound { $[Mo(\eta-C_7H_7)(dppe)Cl]PF_6$ }, 7 (0.2 g, 0.26 mmol) was treated with anhydrous lithium iodide (0.5 g, 3.7 mmol) in acetone (10 cm³). Orange-yellow crystals separated and after 4 h these were collected, washed with ethanol and dried *in* vacuo, ca 75%.

Bis - 1,2 - (diphenylphosphino)ethane(n - cyclohepta - trienyl)bromomolybdenum hexafluorophosphate, 11

The compound was prepared from 3 and 1,2dibromoethane as described for the chloro analogue 7, ca 90%.

Bis(1,2 - bis(diphenylphosphino)ethane)(η - cyclo - heptatrienyl)molybdenum hexafluorophosphate, **12**

The compound

 $\{[Mo(\eta-C_7H_7)(\eta-C_6H_5Me)]PF_6\}$

(0.4 g, 0.94 mmol) and dppe (1.0 g, 2.54 mmol) in ethanol (150 cm³) were heated at 60°C for 24 h. The mixture was cooled to room temperature and pink crystals separated together with white crystals of dppe. The solid was separated and washed with diethyl ether (2×20 cm³) and the residue was recrystallised from acetone: ethanol mixture. The red crystals were collected, washed with diethyl ether and dried *in vacuo*, 0.6 g, 50%.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)hydridomolybdenum, **13**

The compound Na[AlH₂(OCH₂CH₂OMe)₂] (0.6 cm³ of a 70% solution in benzene, 2.08 mmol) was added to [Mo(η -C₇H₇)(dppe)I] (1.0 g, 1.41 mmol) in toluene (30 cm³) and the mixture was heated to 90°C for 1.5 h. The initially brown solution became red and, after cooling to room temperature, water (0.5 cm³) was added. The toluene layer was separated and concentrated under reduced pressure. Addition of petroleum ether (100–120°C) gave red rhombic crystals which were collected and washed with cold petroleum ether (30–40°C) and dried *in vacuo, ca* 73%. The compound is pyrophoric in air.

Bis - 1,2 - (diphenylphosphino)ethane(η - cyclo - heptatrienyl)methylmolybdenum, 14

Methyl-lithium (1.6 cm³ of a 1.9 M solution in diethyl ether, 3.05 mmol) was added to $[Mo(\eta-$

 C_7H_7)(dppe)[] (0.2 g, 0.28 mmol) in tetrahydrofuran (40 cm³). The mixture rapidly became red. It was warmed to 65°C for 15 min and then the solvent was removed under reduced pressure. The red residue was extracted with toluene (2 × 20 cm³) and wet diethylether (5 cm³) was added. Concentration of the mixture and addition of petroleum ether (100– 120°C) (20 cm³) gave deep red prism crystals. These were collected, washed with petroleum ether (30– 40°C) and dried *in vacuo*, 0.07 g, *ca* 42%. The mass spectrum show a parent ion peak at m/e = 602.

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